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NEW USES FOR ANIMAL BY-PRODUCTS

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Bio: Based at USDA's Beltsville Area Research Center, Justin Barone has served as a Research Chemist since 2002 with research focusing on bio-based technologies from agricultural waste products. Before moving to the USDA in 2002, Justin worked in a variety of capacities in industry and academia. Justin was raised in New Jersey and graduated with a B.S. in Materials Science and Engineering from Lehigh University in 1994. In 2000, he received a PhD degree in Macromolecular Science from Case Western Reserve University. He has received recognition for his work on making value added products from animal by-products including making plastic materials from waste poultry feathers.

Speech Summary: It is well known that proteins are abundant in food and are vital to nutrition and biochemical function. What is not very well known is that proteins derived from agricultural sources are used in everyday products such as glue and textiles. Research continues to find new uses for proteins in a wide variety of applications, most of which would be replacements for petroleum-derived materials. Proteins can be a viable source of polymers for fiber, molded plastics, films, and an array of products currently supplied by the synthetic polymers industry. The big advantages are that proteins are derived from a sustainable resource and can be processed in much the same way as conventional synthetic polymers. While there are many current and future non-food uses for proteins, it is the intent of this presentation to concentrate on recent advances focusing on uses as polymers, which have enormous commercial potential.

There are over 2 billion pounds of dry poultry feathers available annually. Domestically, these poultry feathers usually find their way into animal feed known as "feather meal". Profit margins on feather meal are small or nonexistent but rendering the feathers into feed is an efficient disposal method. Feathers are composed of the structural protein keratin, which is a high performance polymer or plastic. Research at USDA's Beltsville Agricultural Research Center (BARC) has shown that fibers obtained from cleaned poultry feathers can be used to make water and air filters, insulation, and reinforcements for polymer composites ('fiberglass' analog). By controlling the *nanostructure*, it is possible to convert the entire feather into a polymer with properties similar to currently available commodity plastics such as polyethylene (PE) and polypropylene (PP).

Non-biodegradable petroleum-based polymers account for about 11% of the 229 million tons of municipal solid waste generated in the U.S. each year, most of which is packaging. With petroleum prices rising (prices are 50-100% more than 1-2 years ago) and "tipping" or land-filling fees rising in densely populated places like the Northeast U.S., packaging that is bio-based and biodegradable has a distinct advantage. This presentation shows the potential of this poultry feather-based polymer and the results of current pilot scale trials in anticipation of creating a commercial product for the agricultural industry such as mulching film or nursery containers.

Biology Basics

Plants and animals are made up of proteins, carbohydrates, nucleic acids, lipids, and water. Proteins usually comprise major structural components in animals like muscle, joints, skin, hair, and nail. Carbohydrates in animals usually combine with proteins to form secondary structures in structural components or form primary structures like shell. In plants, carbohydrates form the primary structural components and proteins play a secondary role. Nucleic acids are DNA and RNA and contain our unique genetic information. Lipids are fats or fatty acids and are mostly hydrocarbon in chemical structure. Biologically, it is essential to have water intimately attached to proteins, carbohydrates, and nucleic acids for them to function properly.

Relating Agricultural Production to Biology

The products of agriculture are obviously biologically based. More importantly, the *by-products* of agriculture are also biologically based. Poultry producers sell meat and the most profit is generated from the breast meat. However, the meat only represents about half of the weight of the chicken. What about the feathers, blood, fat, and other parts not sold? There were 46.92 billion pounds live weight of chickens slaughtered in the U.S. in 2004. Of that, 7% was fat, 7% protein, 3% blood (protein), 3.7% feathers, 26% water, and the balance of 53.3% was meat that was sold in the supermarket. So there was 3.29 billion lb of poultry fat (437,684,314 gallons), 1.74 billion lb of dry feathers, 3.29 billion lb of rendered protein, and 1.4 billion lb of blood available from poultry processing. Similar by-products such as whey protein following cheese making and chitin from shrimp and crab shells exist from other agricultural processing. Fat is a useful lipid molecule that can be converted to fuel such as biodiesel or hydrocarbon chemical intermediates. Feathers, blood, and whey are all proteins. Chitin is a robust carbohydrate molecule. All of these molecules are known as *polymers*. Commercial synthetic polymers are known as *plastics*. Therefore, the by-products of agriculture can be important polymer feedstocks for plastics. Historically, most research has concentrated on carbohydrates like starch probably because they are very abundant in nature. Carbohydrate molecules are not very versatile and only offer hydroxyl (oxygen-hydrogen, -OH) functionality or, in the case of chitin, amide (nitrogen-hydrogen, -NH) functionality also. Functionality refers to the nature of the chemical groups in the molecule and how easily they can be altered to produce a new product. The more diversity in functional groups there is, the more possibility there is to alter the molecule easily. This is an efficient route to use the molecules as feedstocks for chemicals and plastics. The biggest problem for carbohydrates is that the hydroxyl functionality means they soak up a lot of water. This limits the usefulness of the product made from them.

Proteins could be a much better feedstock and are pretty plentiful. Proteins are comprised of twenty different amino acids that offer many functionalities including hydroxyl, amide, thiol (sulfur-hydrogen, -SH), carbon ring, and acid (carbon-oxygen-oxygen-hydrogen, -COOH) groups. The amino acids combine into large protein molecules (primary structure) that then assemble into larger structures such as helices and sheets (secondary structure). The amount of secondary structure usually determines the final properties of the protein such as strength and flexibility. The secondary structure also determines the solubility of the protein.

Feather Keratin

There are about 2 billion pounds of dry feathers available annually in the U.S. as a result of poultry production. Currently, the feathers are cooked and ground into a product called “feather meal” that is sold as animal feed at little or no profit. Feathers not rendered into feather meal are disposed. Concerns over “mad cow” disease or avian flu could induce regulatory pressure to stop feeding animal waste back to animals. In this case, disposal of rendered animal products would become an expensive problem and for sure drive up the cost of poultry in the super market.

Poultry feather is entirely composed of the structural protein *keratin*. Biological evolution has demonstrated that keratin persists in hair and feathers (features that protect the animal), hooves (a feature that bears the animal’s load), and horns (a feature that both protects and supports the animal) because it is tough, strong, and lightweight. Feather keratin is highly crystalline resulting in a stiffness of 5-10 GPa and a strength of 200 MPa. It is also very light with a density of about 0.89 g/cm^3, with the density of water being 1 g/cm^3. Feather keratin is stronger and lighter than high volume synthetic polymers PE and PP.

Poultry feathers have a long, hard, clear quill with small fibers extending from it. The fibers are about 10-25 mm long and have a well-defined diameter of 5 microns (μm). To date, USDA-ARS has shown that the fiber can be disconnected from the quill and used to make: non-woven mats for air and water filtration and insulation; non-woven mats that can be impregnated with polymer resin to make boards and composites; and short fibers for reinforced composites, i.e., “fiberglass”-like materials. USDA-ARS has also used the chopped quill to make reinforced composites. Composites are an interesting material because most plastics sold in the U.S. come with additives that add strength and stiffness to the material and current additives are usually calcium carbonate or glass. While these materials offer higher stiffnesses, they usually add significantly to weight as calcium carbonate and glass are 2-3 times heavier than chopped feather material.

In another application, the entire feather has been chemically converted into hydrolyzed protein for use in cosmetics and consumer products. However, the most interesting and possibly most cost effective and attractive application is to convert the entire feather to bio-based keratin plastics.

Feather Keratin Polymers

Several hundred billion pounds of petroleum-based polymers are sold worldwide each year. At several billon pounds, polymers based on feather keratin would be a niche market at best. However, a few great markets may exist for feather keratin polymers. Small-sized, high volume production parts made of feather keratin for automobiles could help the industry lower vehicle weight and use more bio-based material. Large-sized, low volume mulching films used by vegetable farmers could help the industry solve labor and disposal problems by making the films biodegradable and eliminating the need to collect them at the end of growing seasons. Nursery containers made from feather keratin would afford the short-term stability and long-term biodegradability needed by the nursery industry to dispose of billions of nursery pots each year. Low volume natural polymers needed by the pharmaceutical industry could be well served by feather keratin for tissue engineering substrates or drug delivery materials and sell for dollars per pound.

It is easy to convert feathers into useful polymeric products using techniques currently embraced by the chemical processing industry. Typically, the feathers are cleaned, ground, and mixed with water and glycerol as processing aids. Glycerol is naturally-derived from fatty acids and is employed to keep the materials completey bio-based. Sometimes, redox reagents such as sodium sulfite can be used to aid processing. The powdery mixture is then extruded through a typical polymer extruder to obtain material for pelletizing for further processing or to obtain extruded sheets. The pellets can be further molded into any shape just like traditional petroleum-based plastics. Depending on formulation and processing conditions, the polymers can have stiffness values from 0.04-0.4 GPa or larger, which is typical of high volume commodity plastics such as PE and PP. The density of such polymers is also comparable to PE and PP. However, products made from feather keratin would be sustainable and environmentally-friendly because they are not derived from petroleum and they are biodegradable through natural environmental processes.

Technology Transfer

<u>Phase I.</u> In 1998, USDA-ARS scientists were granted a patent (U.S. Patent #5,705,030) for a process that efficiently cleaned and sanitized feather waste and separated it into useable fiber and quill fractions. Foreign patents were applied for and awarded. Three companies licensed the technology (Featherfiber® Corp.,

Tyson Foods, Inc., and Maxim LLC) and Featherfiber® Corp. of Nixa, MO was successful in building a pilot plant. "Phase I" of the feather technology transfer was to create a clean, useable feather feedstock that could be provided to manufacturers for testing and this was accomplished several years ago.

Phase II. The objective for "Phase II" of technology transfer was to use the feather keratin fiber and quill in value-added products. On pilot and commercial scales, it was demonstrated that products including filters, mats, home insulation, automobile headliner, automotive polymer composites, construction boards and composites, pressed fiber nursery flats, and hydrolyzed keratin for cosmetics could be made. USDA-ARS further developed technology for composites and applied for a patent on the process.

During Phase II, USDA-ARS developed a novel process to convert the poultry feather (quill and fiber indiscriminate) into the useable polymers described above. USDA-ARS applied for and was awarded a patent (pending) on the material and process. Working further with Tyson Foods, Inc. under a cooperative research and development agreement or "CRADA", it was shown that the polymer had potential markets in packaging, mulching films, and nursery containers. Pilot scale extrusion and molding operations were successful in producing large sheets and molded containers. The price of these polymers was projected at about $0.50/lb which, until recently was expensive. For instance, in 2004, low density polyethylene (LDPE) a lower grade plastic used for packaging and film, was selling for about $0.40/lb, making feather keratin polymers too expensive. However, this same LDPE is now selling for $0.60/lb or more because its production is highly dependent on petroleum-based feedstocks and natural gas-fired plants. Feather keratin can be produced on extrusion equipment that is running at temperatures that are 30%-50% colder than temperatures used to process PE and PP so less energy is required as an input. Current development focus is now on analyzing markets and preparing optimal feather keratin polymer formulations for large-scale production.

Recently, USDA-ARS has explored use of feather keratin polymers for textile fibers. Fibers for textiles can be divided into two categories: natural and synthetic. Natural fibers are valued for their breathability, comfort, and low cost. However, most natural fibers tend to soak up a lot of water, except for wool, which tends to be uncomfortable. In addition, natural fibers come in defined diameters (denier) and lengths limiting weaving options. Synthetic fibers can be spun into any diameter and length, can completely repel water, but are very uncomfortable. Smaller diameter natural fibers are usually more expensive but smaller diameter yields higher quality fabrics. Water repellency is important for athletic apparel, which sells for a premium price and is still produced domestically. Novel weaving patterns, like "Polar Fleece", can make synthetic fibers more comfortable to wear. Making fibers from feather keratin polymer would provide the comfort of natural fibers but the spinning versatility of synthetic fibers.